

REMARKS

Claims 1-20 and 22 are pending in the application. Claims 18-20 and 22 have been cancelled by this amendment. New claims 23-25 have been added. Therefore, claims 1-17 and 23-25 are at issue.

Support for new claims 23-25 can be found in the specification, for example, page 5, lines 24-28; page 10, lines 1-3; page 11, line 18; page 12, lines 9-13; page 13, lines 8-11; and Example 5, at pages 19-21.

The examiner has indicated that no certified copy of the priority documents have been received. However, the present application is a §371 application of PCT Application No. PCT/EP05/003009. The priority document was filed during the international phase of the application. See Notice of Acceptance of Application under 35 U.S.C. §371 mailed on July 13, 2007, clearly stating that the priority documents have been received. In view of the above, it is requested that the examiner acknowledge foreign priority in the next communication in connection with the above-identified application.

Claims 1-6 stand provisionally rejected based on the judicially-created doctrine of obviousness-type double patenting over claims 1-6 of copending application No. 11/082,276 ('276 application).

The present application has a filing date (March 22, 2005) preceding that of the '276 application (March 24, 2005). Accordingly, applicants respectfully request that the provisional obviousness-type double patenting rejection of claims 1-6 over claims 1-6 of the '276 application be held in abeyance at least until (and if) the '276 application receives a notice that claims 1-6 therein have been allowed. See MPEP §804 ("The "provisional" double patenting rejection should continue to be made by the examiner in each application as long as there are conflicting claims in more than one application unless that "provisional" double patenting rejection is the only rejection remaining in at least one of the applications."). If the '276 application does not receive a Notice of Allowance prior to a time at which the pending claims in this application are found allowable (but for the presence of the provisional obviousness-type double-patenting rejection), applicants respectfully request a withdrawal of the obviousness-type double patenting rejection from this application.

Claim 1 stands rejected under 35 U.S.C. §103 as being obvious over Tomalia et al. U.S. Patent Publication No. 2001/0011109 ('109 publication) in view of a Moore et al. publication (Moore). Applicants traverse this rejection.

Claim 1 has been amended to clarify the claimed invention. In particular, claim 1 has been amended to recite swellable hydrogel-forming polymer particles comprising hydrogel-forming polymer particles, i.e., superabsorbent (SAP) particles, having at least one hydrophilic polymer of dendritic structure (dendritic polymer) and at least one water-insoluble phosphate present on the surfaces of the particles. The claim amendments are fully supported by the specification, for example, in Example 5 at pages 19-21.

Example 5 also provides an excellent description of the invention recited in independent claim 1 and dependent claims 2-17 and 23-25. In particular, the example discloses the preparation of SAP particles from a monomer solution containing partially neutralized acrylic acid (specification, page 19, line 41 through page 20, line 6). The SAP particles are dried, then sized to a desired particle size range by sieving (specification, page 20, lines 8 and 9). The SAP particles then are surface-postcrosslinked, wherein the postcrosslinking solution contains a dendritic polymer (BOLTORN H40) and tricalcium phosphate (specification, page 20, lines 29-36). The postcrosslinking solution is sprayed onto the SAP particles to position the dendritic polymer and water-insoluble phosphate on the surfaces of the SAP particles (specification, page 20, lines 40-41). The dendritic polymer and water-insoluble phosphate can be applied to the SAP particle surfaces in the same manner in the absence of a surface postcrosslinker (specification, page 5, lines 30-35, for example).

Postcrosslinked SAP particles are illustrated in the attached Exhibit A, i.e., page 97 from *Modern Superabsorbent Polymer Technology*, T. Buchholz et al. eds. (1998). Fig 3.9 of page 97 illustrate the positioning of the dendritic polymer and water-insoluble phosphate on the surfaces of the SAP particles, with or without surface postcrosslinking.

The swellable hydrogel-forming polymer particles of the present claims therefore comprise (a) an SAP particle, (b) a dendritic polymer, and (c) a water insoluble phosphate, wherein both (b) and (c) are present on the surface of the SAP particle.

The nanocomposites of the '109 publication are substantially different from the claimed swellable hydrogel-forming polymer particles, and fail to render the present swellable hydrogel-forming polymer particles obvious under 35 U.S.C. §103.

To establish a *prima facie* case of obviousness, three requirements must be satisfied. First, as the U.S. Supreme Court held in *KSR International Co. v. Teleflex Inc. et al.*, 127 S.Ct. 1727 (2007), "a court must ask whether the improvement is more than the predictable use of prior art elements according to their established functions. ...it [may] be necessary for a court to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person having ordinary skill in the art, all in order to determine whether there was *an apparent reason* to combine the known elements in the fashion claimed by the patent at issue. ...it can be important to *identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements* in the way the claimed new invention does... because inventions in most, if not all, instances rely upon building blocks long since uncovered, and claimed discoveries almost of necessity will be combinations of what, in some sense, is already known." (emphasis added, *KSR, supra*). Second, the proposed modification of the prior art must have had a reasonable expectation of success, determined from the vantage point of the skilled artisan at the time the invention was made. *Amgen Inc. v. Chugai Pharm. Co.*, 18 USPQ2d 1016, 1023 (Fed. Cir. 1991). Lastly, the prior art references must teach or suggest all the limitations of the claims. In *re Wilson*, 165 USPQ 494, 496 (C.C.P.A. 1970).

As recently articulated by the Court of Appeals for the Federal Circuit in *Ortho-McNeil Pharmaceutical Inc. v. Mylan Laboratories Inc.*, 86 USPQ 2d, 1196, 1201-2 (Fed. Cir. 2008):

"As this court has explained, however, a flexible TSM test remains the primary guarantee against a non-statutory hindsight analysis such as occurred in this case. *In re Translogic Tech., Inc.* 504 F.3d 1249, 1257 [84 USPQ 2d 1929] (Fed. Cir. 2007) ("[A]s the Supreme Court suggests, a flexible approach to the TSM test prevents hindsight and focuses on evidence before the time of invention.)."

The '109 publication is directed to nanocomposites of dendric polymers wherein an inorganic reactant is localized with respect to a dendric polymer. The reference fails to teach or suggest, or even consider or address, SAPs.

In particular, the '109 publication discloses a process to prepare aqueous solutions of salts that are normally water-insoluble (paragraph [0108]). The process is exemplified for water-insoluble phosphates in example VIII/5 (paragraph [0290]). In a first step, an aqueous solution was prepared using a water soluble uranyl acetate salt ($\text{UO}_2(\text{CH}_3\text{COO})_2$). In a second step, a dendritic polymer was added to form a complex with the metal compound of the water soluble uranyl salt. In a third step, another salt was added, i.e., a *water* soluble phosphate salt (Na_3PO_4). In the solution containing dendritic polymers, uranyl cations and phosphate anions coexist without precipitation. In the absence of a dendritic polymer, water-insoluble $(\text{UO}_2)_3(\text{PO}_4)_2$ is formed.

The disclosure of the '109 publication cannot be extended to include a *water-insoluble* phosphate salt in the third step. The purpose of Example VIII/5 of the '109 publication, and the '109 publication in general, is to provide a uranyl phosphate *solution*. If a water insoluble phosphate was used, phosphate ions would not be available to form a solution because the insoluble salt would not dissolve. Accordingly, using a water insoluble phosphate in place of the water soluble phosphate destroys the teachings of the '109 publication. The object of the '109 publication is to provide solution of otherwise insoluble salts, as set forth in Example VIII/5 and paragraph [0108].

Although the secondary Moore publication teaches soluble and insoluble metal phosphates, persons skilled in the art would not "immediately envision insoluble metal phosphates" for use in the method disclosed in the '109 publication. To the contrary, persons skilled in the art would *avoid* water insoluble salts because insoluble salts do not provide the anion, e.g., phosphate, in sufficient amounts in solution to even make the '109 publication nanoparticles.

Neither the '109 publication nor the Moore publication remotely teaches or suggests hydrogel forming polymer particles. At paragraph [0113] of the '109 publication, the reference states that the nanocomposites can be further *transformed* into clusters, gels,

networks, and other useful macromolecular structures. This disclosure merely discloses a form into which the nanocomposites can be formed. It does not relate to a nanocomposite that can absorb several times its weight of aqueous sodium chloride (see present specification, page 1, lines 22-25), as presently claimed.

In view of the above, a *prima facie* case of obviousness of claim 1 over a combination of the '109 and Moore publications cannot be established. First, the '109 publication is directed to nanocomposites of dendritic polymers. The nanocomposites allow water solubilization of previously insoluble salts. The nanocomposites are neither water absorbent nor water swellable, and the '109 publication is silent with respect to SAPs. Further, the '109 publication teaches the use of water soluble phosphates, and persons skilled in the art would not substitute an insoluble phosphate disclosed in the Moore publication for the soluble phosphate of the '109 publication because the teachings of '109 publication would be destroyed. A combination of the '109 and Moore publications therefore provides no apparent reason for a person skilled in the art to combine the elements in the way the claimed invention does, i.e., there is no apparent reason from the combination of references to substitute a water insoluble phosphate for the water soluble phosphates of the '109 patent.

In addition to the above, the combination of references fail to teach or suggest all of the presently claimed features. Neither reference is remotely related to swellable, hydrogel forming SAP particles. The nanocomposites of the '109 publication do not absorb large amounts of water, but render insoluble salts soluble. The Moore publication merely discusses phosphate salts. Furthermore, the nanocomposites of the '109 publication are substantially different in form from the presently claimed particles that have a dendritic polymer and a water insoluble phosphate on the surfaces of the particles.

Accordingly, it is submitted that the rejection of claim 1 under 35 U.S.C. §103 as being obvious over the '109 publication in combination with the Moore publication is in error, and should be withdrawn.

Claims 1, 4, 6, and 8-17 stand rejected under 35 U.S.C. §103 as being obvious over Goldman et al. U.S. Patent No. 5,562,646 ('646) in view of Hedstrand et al. U.S. Patent 5,560,929 ('929) and Kobayashi et al. U.S. Patent No. 5,489,469 ('469).

The '646 patent discloses an absorbent core containing a hydrogel forming absorbent polymer, i.e., an SAP. The absorbent core can further contain fibrous materials, such as cotton, kemp, flax, synthetic fibers, etc., as set forth at columns 23-26 of the '646 patent. The '646 patent fails to teach or suggest *any* dendritic polymers. Furthermore, the SAP and fibrous materials of the '646 patent are discrete materials that are simply admixed and retain their individual identities.

The examiner states that the hydrophilic polymer of the '646 patent is selected to provide the desired fluid properties (column 23, lines 50-55). However, the full teachings of the '646 patent is that (a) hydrophilic or *hydrophobic* fibers can be selected, (b) it is the fluid properties of the SAP-fiber *mixture* that is influenced, *not* the properties of the SAP particles *per se*, as in the present invention, and (c) *no* dendritic polymers are even considered in the '646 patent, as admitted by the examiner.

The examiner also admits that the '646 patent fails to teach or suggest including water insoluble phosphates. In fact, the '646 patent merely discloses standard SAP particles admixed with fibrous materials for use in an absorbent core. The SAP disclosed in the '646 patent at columns 9-12 are standard SAP particles, and the '646 patent does not teach or suggest the presently claimed particles, i.e., SAP particles having a dendritic polymer and water insoluble phosphate on the surfaces thereof.

The examiner relies upon the '929 patent for a teaching of a dendritic polymer useful as a gel, which he asserts would enhance the absorbency of the absorbent core of the '646 patent. This reasoning is incorrect.

The '929 patent is directed to *hydrophobic* dendritic polymers capable of associating or chelating with metal ions (see '929 patent, abstract). Also set column 3, lines 18-30, of the '929 patent, where it is disclosed that the dendritic polymers are useful for extracting metal ions from aqueous solution into non-aqueous solutions "containing these structural copolymers". The '929 patent fails to teach or suggest *hydrophilic* dendritic polymers, as presently claimed.

The '929 patent states that the dendritic polymers can be used in the formation of an aqueous/organic gel, i.e., the dendritic polymers can be admixed with other ingredients to form a gel. The disclosure of column 1, lines 35-38 does not teach that the disclosed dendritic polymers form a gel on contact with water. If gel formation *per se* occurs at all, it would be in a *hydrophobic* solvent, not water, because of the hydrophobic nature of the dendritic polymers of the '929 patent.

In view of the *highly* hydrophobic nature of the dendritic polymers of the '929 patent, and their disclosed capability of extracting metal ions into a non-aqueous solutions, persons skilled in the art would have had absolutely no motivation to include a dendritic polymer in the absorbent core of the '646 patent with any expectation of providing a core having an enhanced absorbance for aqueous liquids. In fact, due to the hydrophobic nature of the disclosed dendritic polymer of the '929 patent, persons skilled in the art would *avoid* adding a dendritic polymer to the core of the '646 patent. In addition, persons skilled in the art would have had no incentive to position a hydrophobic dendritic polymer on an SAP particle because a *decrease* in aqueous fluid absorbance would be expected, i.e., the hydrophobic surface would repel water from the SAP particle.

The '469 patent is directed to SAP particles having a fibrous material and an inorganic material on the surface of the particle. The '469 patent fails to teach or suggest any dendritic polymer.

In view of the above, a *prima facie* case of obviousness of independent claim 1 over a combination of the '646, '929, and '469 patents cannot be established. The '646 patent is directed to a mixture of a standard SAP and a fibrous material. The reference fails to teach or suggest a dendritic polymer, let alone positioning the dendritic polymer on the surfaces of SAP particles. The '469 patent likewise is completely silent with respect to dendritic polymers or their combination with an SAP.

The '929 patent is directed to dendritic polymers, but for use in extracting metal ions from an aqueous to a nonaqueous solution. The dendritic polymers of the '929 patent are specifically disclosed as being hydrophobic, no hydrophilic dendritic polymers are disclosed. The dendritic polymers of the '929 patent can be *formulated* into gels, but do not

form gels when contacted in water, and actually cannot form gels in aqueous solutions because they are hydrophobic.

Accordingly, persons skilled in the would have had no apparent reason to include a dendritic polymer of the '929 patent with the SAPs either the '646 or '469 patents. Contrary to the reasoning provided by the examiner, the inclusion of a hydrophobic dendritic polymer on the surfaces of an SAP particle, as claimed, could not be reasonably expected to increase absorbency of the particle. In fact, it would be expected that absorbency would decrease because the *hydrophobic* dendritic polymer would provide at least a partial barrier between contact of an SAP with water.

For all the reasons set forth above, it is submitted that independent claim 1 would not have been obvious over a combination of the '646, '929, and '469 patent, and that the rejection of claim 1 under 35 U.S.C. §103 should be withdrawn. It is further submitted that because claim 1 would not have been obvious, the rejection of dependent claims 4-6 and 8-17 under 35 U.S.C. §103 over this combination of references also should be withdrawn.

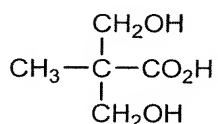
Claims 2 and 3 stand rejected under 35 U.S.C. §103 as being obvious over the '646 patent in view of the '929 and '469 patents, and in further view of Tomalia et al. U.S. Patent No. 4,507,466 ('466). Claim 7 stands rejected under 35 U.S.C. §103 as being obvious over the '646 patent in view of the '929 and '469 patents, and in further view of Chen et al. U.S. Patent No. 6,261,679 ('679). Applicants traverse these rejections.

First, these claims recite preferred embodiments of the present invention. Applicants do not rely solely on the features recited in claims 2, 3, or 7 for patentability, but rely upon the features recited in these claims *and* in independent claim 1. Applicants have demonstrated the patentability of claim 1 above, and the quaternary '466 and '619 patents do not negate the patentability of independent claim 1. Therefore, it is submitted that claims 2, 3, and 7 are patentable for the same reason claim 1 is patentable, and the rejections of these claims should be withdrawn.

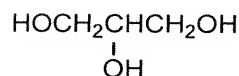
With further respect to claims 2 and 3, the '466 patent is directed to the dendritic polymers having increased terminal group densities, and therefore a greater and

more uniform reactivity ('466 patent, abstract). The examiner also misrepresents the dendritic polymer disclosed at column 9, lines 19-45, and particularly, at lines 33-35. The '466 patent teaches reacting a "polyamidoamine dendrimer" (column 9, lines 29-30) with an α , β -ethylenically unsaturated ester to form a polyester. See the structure in the '466 patent at the top of columns 11 and 12, for example; particularly noting that the polyester contains a plurality of a nitrogen atoms as amide and as amino groups.

The claimed dendritic polymer formed from a polyol and 2,2-dimethylolpropionic acid has a vastly different structure from the dendritic polymer of the '466 patent, and is prepared in a vastly different manner, e.g., contains *no* nitrogen atoms as amide *or* amino groups.



2,2-dimethylolpropionic acid



(see present specification page 4, line 21-29)
a polyol

Accordingly, the combination of references, including the '466 patent, fails to teach or suggest every claimed element, and the references provide no apparent reason for a person skilled in the art to modify the structure of disclosed nitrogen-containing dendritic polymer in a manner to arrive at the claimed dendritic polymer.

With respect to the examiner's comment that no unexpected results were demonstrated for the claimed dendritic polymer and that this feature is "arbitrary and obvious", applicants point to Table 1, at page 22, wherein the *combination* of a claimed dendritic polymer and claimed water-insoluble phosphate (Example 4) provided unexpected and unpredicted improvements (see SFC values, for example) over Examples 1-3, which included neither or only one of the dendritic polymer and water insoluble phosphate. Also see Examples 5 and 6. The dendritic polymer used in the present examples is BOLTORN[®] 40. See attached Exhibit B, i.e., WO 2008/071575, pages 4 and 5, for the structures of a dendritic polymer recited in claims 2 and 3. Also note the substantial difference in structure

between the BOLTORN[®] polymer as recited in claims 2 and 3 and the structure of the dendritic polymer of the '466 patent.

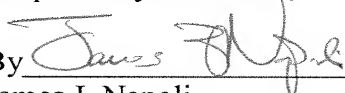
With further respect to claim 7, the hollow spheres of the '679 patent are utilized to prepared foams by including the hollow spheres in the structural matrix, then breaking the spheres to create open cells. The presently claimed SAP particles are not foams, and the hollow microspheres are on the surfaces of the particles and are not broken to form open cells. The use and structure of the hollow microspheres of the '679 patent are completely different from the claimed use.

It is submitted that all claims are in a form and scope for allowance. An early and favorable action on the merits is respectfully requested.

Should the examiner wish to discuss the foregoing, or any matter of form in an effort to advance this application toward allowance, the examiner is urged to telephone the undersigned at the indicated number.

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Respectfully submitted,

By 

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MODERN SUPERABSORBENT POLYMER TECHNOLOGY

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Preface

Acknowledgments

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1 Absorbency and

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1.1. Absorbents /

1.1.1. Tradition

1.1.2. Physics

1.2. Superabsorbents

1.2.1. Physics

1.2.2. Superabsorbents

1.2.2.1

1.2.2.2

1.2.2.3

1.3. Composite Absorbents

2 Chemistry of Superabsorbents

Thomas L. Staples

2.1. Preparation of Superabsorbents

2.1.1. Examination of

Acrylic

2.1.2. Examination of

Partial

2.2. Free-Radical Polymerization

Related Monomers

2.2.1. Monomers

2.2.2. Storage

selected to minimize handling and disposal. Sorbent manufacturing needs to be managed by screening. That is, two paths are dis-

product or to include path is not discussed. Fine particles are recycled into the process (direct from blended product).^{14,15} Fines are blended. Fines are substantial agglomerates. Mixing of the hydrate with the addition of recycle fines to a gel cycle of fines to a gel cycle of a few parts of water rated fines and fresh fines having sufficient

the gel, for example, fines are not chemically. It may not retain its swelling the swelling of oversized larger particles.

is also described. In addition and the mixture added to the reactor, following monomer mix increases problems were noted. See patents. However, useful at a commercial fines¹⁶ is similar to recycling on a continuous monomer mix.²⁹ It, a nonswelling salt is added to an aqueous solution may be as high as. When fines are recycled to properties of polymers of the same was noted.¹⁷

3.2.8. Addition of Post-Treatments

3.2.8.1. Advanced Products. The processes described above produce a particle with crosslinking that may be assumed to be essentially uniform throughout the particle. As such, the swelling and modulus behavior of the product particles can be described by theories of network swelling and elasticity (see Chapter 5). One problem associated with these superabsorbent polymers was also recognized in a variety of water soluble polymers, e.g., poly(acrylamide), cellulose ethers,⁹⁵ or soluble poly(acrylic acid).⁹⁶ This problem is the tendency of the granular polymers to clump, "gel block," or form fish-eyes when aqueous liquids are added to them or they are added to aqueous liquids. The surfaces of the massed particles swell rapidly to form a soft, deformable layer. The resulting particle deformation and interparticle adhesion reduces interparticle porosity and limits the swelling rate of the polymer mass to the diffusion rate of liquid through the partially swollen mass.

The first attempts to solve this problem in highly absorbent anionic polyelectrolytes used multivalent cations to form a crosslinked surface layer that was more rigid than the original core polymer.⁹⁷ Subsequently, to give products with improved dispersibility and absorption rate, the surface of crosslinked polyacrylate particles was reacted with a variety of multifunctional organic compounds.^{49,50,98,99} This structural improvement is shown schematically in Figure 3.9. Swelling capacity data as a function of particle size readily demonstrate that a shell of real, as opposed to infinitesimal, thickness is formed by surface crosslinking processes. The shell of higher crosslink density provides a more rigid surface layer during swelling and prevents the gel-blocking that would otherwise occur early in the swelling process (Chapter 5). As a result, liquid can flow through the bed of particles to each particle, increasing the effective surface area available for swelling and the apparent swelling rate. The swelling and modulus behavior of structured particles are discussed in Chapter 5.

Because a surface layer is formed on each individual particle, the crosslinking reaction, but not necessarily the reagent addition, must occur after achieving the desired particle size distribution. Any compound that can react with two or more functional groups on the polymer backbone can function as a surface crosslinking reagent. For superabsorbents, this requires reagents that can react with the car-

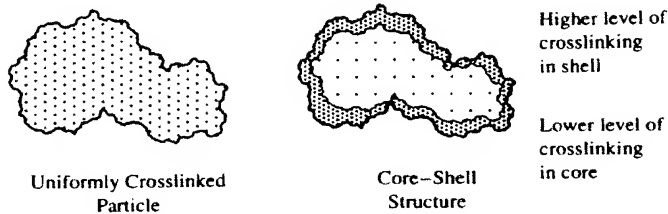


Figure 3.9. Schematic representation of a uniformly crosslinked superabsorbent particle and a structured particle with a surface layer of higher crosslink density.

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(54) Title: FLAME RETARDANT COMPOSITION COMPRISING DENDRITIC POLYMERS

(57) Abstract: The invention relates to a product as obtained by reaction of: a) At least one polyol selected from the group consisting of a linear or branched, trihydric or tetrahydric alcohol and a linear pentahydric or hexahydric alcohol; b) At least one melamine comprising compound; and c) At least one dendritic polymer substituted by hydroxy groups; and to flame retardant compositions comprising these products.



WO 2008/071575 A1

Flame retardant composition comprising dendritic polymers

The invention relates to novel flame retardant compositions comprising dendritic polymers and to the use thereof in polymers, preferably thermoplastic polymers.

Flame retardants are added to polymeric materials (synthetic or natural) to enhance the flame retardant properties of the polymers. Depending on their composition, flame retardants may act in the solid, liquid or gas phase either chemically, e.g. as a spumescent by liberation of nitrogen, and/or physically, e.g. by producing a foam coverage. Flame retardants interfere during a particular stage the combustion process, e.g. during heating, decomposition, ignition or flame spread.

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- US-A-4,010,137* discloses a process for the preparation of a melamine based flame retardant by a reaction in an extruder between a melamine comprising compound and a polyol with the optional addition of a polymeric carrier material. Melamine pyrophosphate and pentaerythritol are combined as single component flame retardants and heated in a vessel at 175°C - 275°C. A clear disadvantage of that process results from the fact that the preparation of the flame retardant requires a process time of at least 0.5 hours and up to 4 hours.

- 20
- A process for the preparation of a melamine based flame retardant is disclosed in *WO 00/68337*. This reference discloses a process wherein powder blends comprising pentaerythritol and melamine phosphate are prepared. These powder blends, however, are strongly limited in their applicability for the manufacture of polymer compositions, which is caused by the fact that foaming occurs during the processing of the powder blend in the polymer, e.g. during the compounding or injection moulding.

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- A severe problem results from the fact that single component flame retardants that contain phosphoric ester groups are subject to hydrolysis. In the event that these flame retardant additives are blended with polymer materials, such as polypropylene, their moisture sensitivity causes considerable leaching of the flame retardant molecules from the polymer matrix resulting in reduced flame retardant efficiency of the polymer composition and decreased electrical insulation properties.

- 30
- Various methods are known to increase the water resistance of polymeric flame retardant compositions. They include partial phosphorylation of polymers, such as polyvinyl acetate, encapsulation of polar flame retardant components, such as acid source APP particles with copolymer of vinyl pyrrolidone and comonomer, modification of flame retardants with surfactants (non-ionic or ionic) or the replacement of polyols (polar species) by other char formers, such as dialkyl tin oxide, dialkyl tin dialkoxide, or polyol(alkylcarbonate).

- 2 -

WO 2004/055029 discloses a process for the preparation of a melamine based flame retardant by a reaction of a melamine comprising compound and a polyol, wherein the melamine comprising compound is selected from the group consisting of melamine phosphate, melamine pyrophosphate and melamine polyphosphate and the polyol is selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol. The reaction is carried out by reactive extrusion in an extruder in a molar ratio of the melamine comprising compound to the polyol between 1.0 : 1.0 and 4.0 : 1.0 and the reaction is performed at a temperature between 200° and 300°C.

The compositions obtained by the prior art process possess limited resistance in a water storage test at elevated temperatures (leaching test).

Object of the present invention is to provide an improved process for the preparation of a melamine based flame retardant and its master batch with high flowability.

A particular object of the invention is the preparation of polymeric flame retardant compositions of increased water resistance while preserving the flame retardant performance (UL94 V-0) and mechanical properties.

These objects are achieved by the invention; which relates to an intumescent flame retardant (INFR) obtainable by a reaction between a melamine comprising compound, a polyol and an additional polymeric component possessing more than 4 OH-functionalities with the optional addition of a polymeric carrier material. The melamine based flame retardant is particularly suitable for producing flame retardant polymer compositions of high water resistance. Due to the higher thermal stability of the melamine-based flame retardant, the polymer composition can be moulded at higher temperatures as compared to the polymer compositions disclosed in *US-A-4,010,137*.

The present invention relates to a product as obtained by reaction of:

- a) At least one polyol selected from the group consisting of a linear or branched, trihydric or tetrahydric alcohol, a linear pentahydric or hexahydric alcohol, a linear or cyclic C₄-C₆aldose and a linear or cyclic C₄-C₆ketose;
- b) At least one melamine comprising compound; and
- c) At least one dendritic polymer substituted by hydroxy groups.

The general terms used in the description of the instant invention, unless defined otherwise, are defined as follows:

A linear or branched, trihydric alcohol is, for example, glycerol or trimethylolethane.

A linear tetrahydric alcohol is, for example, erythritol and its 3 isomeric forms, e.g. D-, L- and meso-erythritol.

A branched tetrahydric alcohol is, for example, pentaerythritol.

5 A linear, penta- or hexa-hydric alcohol is derived, for example, from linear pentitols, such as D(+)- and L(-)-arabitol, adonitol or xylitol, or from linear hexitols, such as D-sorbitol, D-mannitol or dulcitol.

10 A linear or cyclic C₄-C₆aldose and a linear or cyclic C₄-C₆ketose is derived, for example, from C₄aldoses, such as D(-)- and L(+)-erythrose or D(-)- and L(+)-threose, C₅aldoses, such as D(-)- and L(+)-arabinose, D(-)-ribose or D(+)-xylose, C₆aldoses, such as D(+)-glucose, D(+)-mannose or D(+)-galactose, or from a C₆ketose, such as fructose or L(-)-sorbose, and epimeric forms thereof.

15 The term melamine comprising compound comprises within its scope any compound wherein the melamine structure: 1,3,5-triazine-2,4,6-triamine (= cyanuric acid triamide) or condensates thereof are present. The definition applies to monomeric, oligomeric or polymeric compounds of melamine, condensates of melamine or condensates of melamine and phosphoric acid.

20 Preferred melamine comprising compounds are melamine cyanurate, melamine phosphate, dimelamine phosphate, melamine pyrophosphate, melamine polyphosphate, melamine borate, melamine ammonium phosphate, melamine ammonium polyphosphate, melamine ammonium pyrophosphate, melem, melam or melon or polyphosphates of melem, melam or melon.

Melamine comprising compounds of the type mentioned above are known. Some of them are commercially available.

25 A dendritic polymer substituted by hydroxy groups comprises within its scope any dendritic polymer including dendrimers, regular dendrons, dendrigrafts, or hyperbranched polymers. Dendritic polymers, including dendrimers and hyperbranched polymers, can be prepared by condensation, addition or ionic reactions of monomeric units having at least two different types of reactive groups.

30 The preparation and characterization of dendrimers, dendrons, dendrigrafts or hyperbranched polymers is known. Examples of dendrimers and dendrons and methods of synthesizing them are known from *U.S. Patent Specification Nos. 4,507,466; 4,558,120; 4,568,737; 4,587,329; 4,632,337; 4,694,064; 4,713,975; 4,737,550; 4,871,779 and 4,857,599.*

Examples of hyperbranched polymers and methods of synthesizing them are known from *U.S. Patent Specification No. 5,418,301*.

Some dendritic polymers are commercially available, e.g. Perstorp (www.perstorp.com).

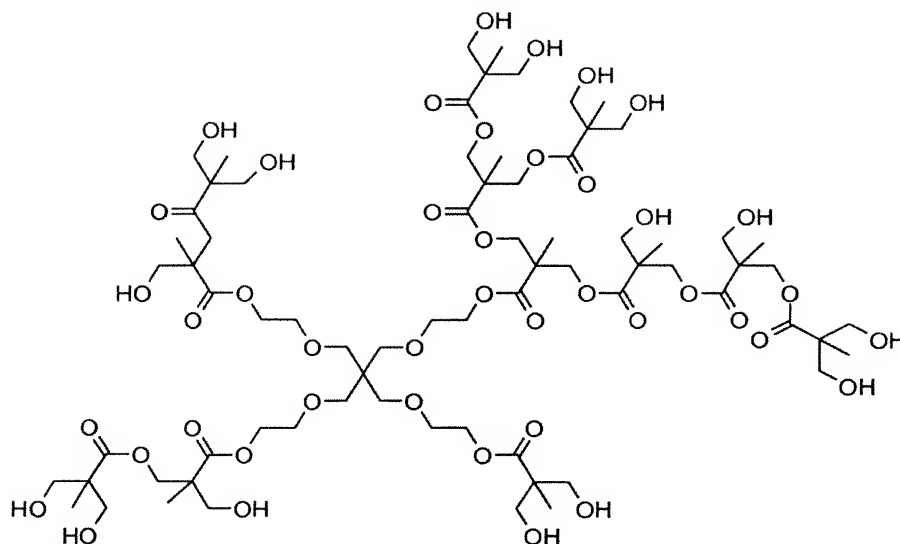
5 Preferred dendritic polymers are dendrimers based on, for example, a polyester, polyether, polythioether, polyamide, polyetherketone, polyalkylene imine, polyamido amine, polyether amide, polyarylene, polyalkylene, aromatic polyalkylene, polyaryl acetylene and/or a phosphorus- or silicon-containing dendrimer or combinations thereof.

10 According to a preferred embodiment, dendritic polymers substituted by hydroxy groups are particularly suitable, which are commercially available from Perstorp under the trademark Boltorn®. These dendritic polymers are of polyester type consisting of a multifunctional core, from which branches extend to give a highly branched inherent structure with a large number of terminal hydroxy groups. The core consists of a polyalcohol, such as trimethylolpropane, pentaerythritol or derivatives thereof. The hyperbranched structure is built from 2,2-dimethylol propionic acid (Bis-MPA). Suitable products are

- 15 • BOLTORN H 20 (16 terminal hydroxy groups, nominal molecular weight 1750 g/mol, amorphous, T_g : 25°C)
- BOLTORN H 2003 (12 terminal hydroxy groups, nominal molecular weight 2300 g/mol, partially fatty acid terminated, T_g : -5°C)
- BOLTORN H 2004 (6 terminal hydroxy groups, nominal molecular weight 3100 g/mol, 20 T_g : -35°C, liquid at room temperature, viscosity 15 Pas at 23°C)
- BOLTORN H 30 (32 terminal hydroxy groups, nominal molecular weight 3600 g/mol, amorphous, T_g : 35°C)
- BOLTORN H 40 (64 terminal hydroxy groups, nominal molecular weight 7300 g/mol, amorphous, T_g : 40°C)

25 A representative structural formula of BOLTORN H 20 is given below:

- 5 -



According to an alternative preferred embodiment, dendritic polymers substituted by hydroxy groups are particularly suitable, as described by *P. Froehling, J. Polymer Science: Part A: Polymer Chemistry, Vol. 42, 3110-3115 (2004)*.

- 5 Suitable dendritic polymers are obtained from the starting reaction of a cyclic anhydride with diisopropanol amine, thus yielding a tertiary amide with one -COOH and two -OH groups, and subsequent polycondensation.

Suitable cyclic anhydrides are cis-1,2-cyclohexane-dicarboxylic anhydride (HHPA), cis-1,2-cyclohex-4-ene-dicarboxylic anhydride (THPA), phthalic anhydride, (PA), succinic anhydride
 10 (SA), 1-oct-2-ene-succinic anhydride (OSA) and glutaric anhydride (GA). Other amines, e.g. diisobutanolamine or dicyclohexanolamine, can be used, too.

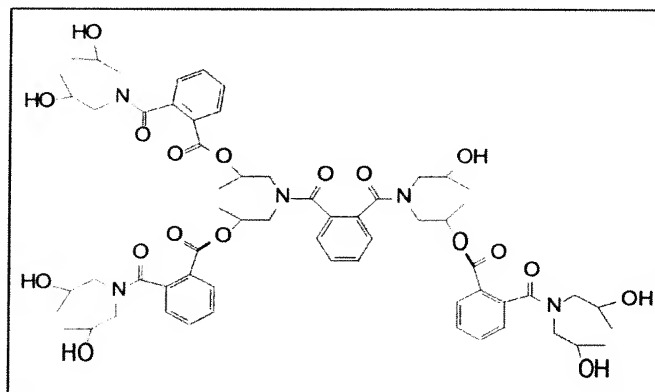
These polymers are commercially available under the trademark Hybrane® from DSM Corporation (DSM HYBRANE, www.dsm.com). HYBRANE polymers have a broad molecular weight distribution. Molecular weights range from 1 000 to 10 000, with a polydispersity of 3-

15 5. Suitable products are:

- HYBRANE P 1000 (phthalic anhydride + diisopropanolamine, 5.5 OH, MW: 800)
- HYBRANE S 1200 (phthalic anhydride + diisopropanolamine, 8 OH, MW: 1200)
- HYBRANE H 1500 (hexahydrophthalic anhydride + diisopropanolamine, 8 OH, MW: 1500)
- 20 • HYBRANE PS 2550 (phthalic anhydride + diisopropanolamine + stearic acid, 4 OH, 4 stearyl, MW: 2500)

- 6 -

A representative structural formula of the core structure of a HYBRANE product obtainable from phthalic anhydride and diisopropanolamine is given below



According to a preferred embodiment, the invention relates to a product as obtained by reaction of:

5

- a) A linear or branched, trihydric or tetrahydric alcohol;
- b) A melamine compound selected from the group consisting of melamine phosphate, melamine pyrophosphate and melamine polyphosphate; and
- c) At least one dendritic polymer substituted by hydroxy groups.

10 According to a particularly preferred embodiment, the invention relates to a product as obtained by reaction of:

15

- a) A tetrahydric alcohol selected from the group consisting of pentaerythritol and dipentaerythritol;
- b) A melamine compound selected from the group consisting of melamine phosphate, melamine pyrophosphate and melamine polyphosphate; and
- c) A dendritic polymer of the polyester or polyamide type substituted by hydroxy groups.

According to a highly preferred embodiment the invention relates to a product as obtained by reaction of:

20

- a) A tetrahydric alcohol selected from the group consisting of pentaerythritol and dipentaerythritol;
- b) A melamine compound selected from the group consisting of melamine phosphate and melamine pyrophosphate; and

- 7 -

- c) A dendritic polymer of the polyester or polyamide type substituted by hydroxy groups.

According to a very highly preferred embodiment, the invention relates to a product as obtained by reaction of:

- 5 a) Pentaerythritol;
 b) Melamine phosphate; and
 c) A dendritic polyester formed from an initiator compound selected from the group consisting of trimethylolpropane, pentaerythritol and ethoxylated pentaerythritol and the chain-extending dimethylolpropionic acid or a polycondensation product
10 of a cyclic carboxylic acid anhydride and diisopropanolamine.

The product according to the invention is obtainable by reactive mixing or compounding methods, particularly reactive extrusion methods, in customary mixing machines, wherein the components a), b) and c) and, optionally, further additives and polymers are mixed and melted. Suitable machines are known to those skilled in the art. They are predominantly mix-
15 ers, kneaders and extruders.

The amounts of components a), b) and c) present in the reaction product may vary within wide limits. A preferred range of component a) is from about 10.0 to 50.0 wt.%, of component b) from about 40.0 - 80.0 wt.% and of component c) of about 0.1 to 10.0 wt.%.

According to a particularly preferred embodiment, the range of component a) is from about
20 15.0 - 40.0 wt%, of component b) from about 50.0 - 75.0 wt% and of component c) of about 0.1 -10.0 wt%.

According to a highly preferred embodiment, the range of component a) is from about 15.0 - 30.0 wt%, of component b) from about 60.0 - 75.0 wt% and of component c) of about 0.1 -10.0 wt%.

25 The product according to the invention is characterized by its excellent thermal stability. In the context of the description of the invention, thermal stability is defined as the degree of resistance against foaming upon heating of the melamine based flame retardant. For a more precise differentiation in thermal stability of flame retardant compositions physicochemical methods, such as thermo-gravimetric analysis (TGA) and differential scanning calorimetry
30 (DSC), can be used.

The reaction of components a), b) and c) can be performed at temperatures between about 100°C and 300°C. However, for a complete conversion the reaction should be performed at temperatures higher than 200°C.

The maximum temperature for the reaction is chosen below 300°C. Preferably, the reaction is carried out in a temperature range between 220°C and 280°C. Between 220°C and 280°C a good balance is obtained between the rate of reaction and the degradation of the reaction product. More preferably, the reaction is conducted at a temperature between 230°C and 260°C. The thermal stability of the melamine based flame retardant produced in this temperature range is excellent.

The time period for reaction is, in general, between 1 minute and 1 hour, preferably 1 and 20 minutes.

The product of the invention is outstandingly suitable for imparting flame-retarding properties to polymers, e.g. synthetic polymers, especially thermoplastics. It has been found advantageous to add polymer material to the extruder as a carrier resin in addition to the components a), b) and c) defined above. A more constant extruder output is achieved with less than 30 weight% of polymer present in the flame retardant composition, especially when the extruder operates at temperatures below 270°C. The amount of the polymer in general should be kept low, e.g. between 5.0 - 30.0 weight, particularly between 5.0 – 20.0%, related to the total weight amount of the flame retardant composition.

In a preferred embodiment of the invention the extrusive reaction of components a), b) and c) is carried out in the presence of a polymer component, particularly 5.0 to 20.0 weight% of a polymer.

Any type of polymer material can be chosen that is suitable for melt processing at the extruder temperature, preferably at processing temperatures below 300°C. In general the polymer or carrier resin is chosen according to the polymer matrix material that needs flame retardation. Polypropylene and polyethylene are the first choice due to its large availability and easy processing properties. It has been found in this respect that through the use of high density polyethylene, HDPE, light coloured melamine based flame retardant pellets can be produced, which is advantageous for producing light coloured, flame retardant polymer compositions. In an alternative embodiment the use of polypropylene has been found advantageous. An acceptable colour of the flame retardant master batches is obtained, combined with high fluidity and excellent flame retardancy and mechanical properties of the composite material. Furthermore through the use of a polymer it is easier to obtain pellets of the melamine based flame retardant.

Other polymers suitable for the polymer composition of the present invention are those polymers, which are processed at temperatures below 300°C and preferably below 280°C.

A further embodiment of the invention is a flame retardant composition, which comprises

A) A product as obtained by reaction of:

- a) At least one polyol selected from the group consisting of a linear or branched, trihydric or tetrahydric alcohol, a linear pentahydric or hexahydric alcohol, a linear or cyclic C₄-C₆aldose and a linear or cyclic C₄-C₆ketose;
- b) At least one melamine comprising compound; and
- c) At least one dendritic polymer substituted by hydroxy groups; and

B) A polymer substrate.

A suitable polymer substrate according to Component B) consists of synthetic polymers, such as:

1. Polymers of mono- and di-olefins, for example polypropylene, polyisobutylene, polybutene-1, poly-4-methylpentene-1, polyvinylcyclohexane, polyisoprene or polybutadiene and also polymerisates of cyclo-olefins, for example of cyclopentene or norbornene; and also polyethylene (which may optionally be crosslinked), for example high density polyethylene (HDPE), high density polyethylene of high molecular weight (HDPE-HMW), high density polyethylene of ultra-high molecular weight (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), and linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE).

Polyolefins, that is to say polymers of mono-olefins, as mentioned by way of example in the preceding paragraph, especially polyethylene and polypropylene, can be prepared by various processes, especially by the following methods:

- a) By free radical polymerisation (usually at high pressure and high temperature);
- b) In the presence of a catalyst. The catalyst usually contains one or more metals of Groups IVb, Vb, Vlb or VIII of the Periodic Table. Those metals generally have one or more substituents or ligands, such as oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls, which may be either π - or σ -coordinated. Such metal complexes may be free or fixed to carriers, for example to activated magnesium chloride, titanium(III) chloride, aluminium oxide or silicon oxide. Such catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be active as such in the polymerisation or further activators may be used, for example metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyl oxanes. This applies particularly to metals of Group(s) Ia, IIa and/or IIIa. The activators may have been modified, for example, with further ester, ether, amine or silyl ether groups. Such catalyst systems are usually referred to as Phil-

lips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or Single Site Catalysts (SSC).

2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).
3. Copolymers of mono- and di-olefins with one another or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/butene-1 copolymers, propylene/isobutylene copolymers, ethylene/butene-1 copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, ethylene/vinylcyclohexane copolymers, ethylene/cyclo-olefin copolymers, for example ethylene/norbornene (COC), ethylene/1-olefin copolymers wherein the 1-olefin is prepared *in situ*, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/vinyl cyclohexene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers, ethylene/acrylic acid copolymers and salts thereof (ionomers), and also terpolymers of ethylene with propylene and a diene, such as hexadiene, dicyclopentadiene or ethylidenenorbornene; and also mixtures of such copolymers with one another or with polymers mentioned under 1), for example polypropylene-ethylene/propylene copolymers, LDPE-ethylene/vinyl acetate copolymers, LDPE-ethylene/acrylic acid copolymers, LLDPE-ethylene/vinyl acetate copolymers, LLDPE-ethylene/acrylic acid copolymers and alternately or randomly structured polyalkylene-carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.
4. Polystyrene, poly(p-methylstyrene), poly(α -methylstyrene).
5. Aromatic homopolymers and copolymers derived from vinyl-aromatic monomers, for example styrene, α -methylstyrene, all isomers of vinyltoluene, for example p-vinyltoluene, all isomers of ethylstyrene, propylstyrene, vinylbiphenyl, vinylnaphthalene, vinylanthracene and mixtures thereof; homopolymers and copolymers can have a syndiotactic, isotactic, hemi-isotactic or atactic stereo structure; preference is given to atactic polymers. Also included are stereo block polymers.
6. Homopolymers and copolymers can have a syndiotactic, isotactic, hemi-isotactic or atactic stereo structure; preference is given to atactic polymers. Also included are stereo block polymers.

- 5 a) Copolymers including the already mentioned vinyl-aromatic monomers and co-
monomers selected from ethylene, propylene, dienes, nitriles, acids, maleic an-
hydrides, maleic acid amides, vinyl acetate, vinyl chloride and acrylic acid deriva-
tives and mixtures thereof, for example styrene/butadiene, styrene/acrylo-nitrile,
styrene/ethylene (interpolymers), styrene/alkyl methacrylate, styrene/butadi-
ene/alkyl acrylate and methacrylate, styrene/maleic anhydride, styrene/acryloni-
trile/methyl acrylate; high-impact-strength mixtures consisting of styrene copoly-
mers and another polymer, for example a polyacrylate, a diene polymer or an
ethylene/propylene/diene terpolymer; and also block copolymers of styrene, for
10 example styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene-
butylene/styrene or styrene/ethylene-propylene/styrene.
- 15 b) Hydrogenated aromatic polymers prepared by hydrogenation of the polymers
mentioned under 6.), especially polycyclohexylethylene (PCHE), often also re-
ferred to as polyvinylcyclohexane (PVCH), which is prepared by hydrogenation of
atactic polystyrene.
- c) Hydrogenated aromatic polymers prepared by hydrogenation of the polymers
mentioned under 6a.).
- 20 7. Graft copolymers of vinyl-aromatic monomers, for example styrene on polybutadiene,
styrene on polybutadiene/styrene or polybutadiene/acrylonitrile copolymers, styrene
and acrylonitrile (or methacrylonitrile) on polybutadiene; styrene, acrylonitrile and me-
thyl methacrylate on polybutadiene; styrene and maleic anhydride on polybutadiene;
styrene, acrylonitrile and maleic anhydride or maleic acid imide on polybutadiene; sty-
rene and maleic acid imide on polybutadiene, styrene and alkyl acrylates or alkyl
methacrylates on polybutadiene, styrene and acrylonitrile on ethylene/propylene/diene
25 terpolymers, styrene and acrylonitrile on polyalkyl acrylates or polyalkyl methacrylates,
styrene and acrylonitrile on acrylate/butadiene copolymers, and mixtures thereof with
the copolymers mentioned above under Paragraph 6, such as those known, for exam-
ple, as so-called ABS, MBS, ASA or AES polymers.
- 30 8. Polymers derived from α,β -unsaturated acids and derivatives thereof, such as poly-
acrylates and polymethacrylates, or polymethyl methacrylates, polyacrylamides and
polyacrylonitriles impact-resistant-modified with butyl acrylate.
9. Copolymers of the monomers mentioned under Paragraph 9 with one another or with
other unsaturated monomers, for example acrylonitrile/butadiene copolymers, acryloni-

trile/alkyl acrylate copolymers, acrylonitrile/alkoxyalkyl acrylate copolymers, acrylonitrile/vinyl halide copolymers or acrylonitrile/alkyl methacrylate/butadiene terpolymers.

10. Polymers derived from unsaturated alcohols and amines or their acyl derivatives or acetals, such as polyvinyl alcohol, polyvinyl acetate, stearate, benzoate or maleate, polyvinylbutyral, polyallyl phthalate, polyallylmelamine; and the copolymers thereof with olefins mentioned in Paragraph 1.
11. Homo- and co-polymers of cyclic ethers, such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.
12. Polyacetals, such as polyoxymethylene, and also those polyoxymethylenes which contain comonomers, for example ethylene oxide; polyacetals modified with thermoplastic polyurethanes, acrylates or MBS.
13. Polyphenylene oxides and sulphides and mixtures thereof with styrene polymers or polyamides.
14. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, such as polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides derived from m-xylene, diamine and adipic acid; polyamide 6/I (polyhexamethylene isophthalamide, MXD (m-xylylenediamine); polyamides prepared from hexamethylenediamine and iso- and/or tere-phthalic acid and optionally an elastomer as modifier, for example poly-2,4,4-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide. Block copolymers of the above-mentioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, for example with polyethylene glycol, polypropylene glycol or polytetramethylene glycol. Also polyamides or copolyamides modified with EPDM or ABS; and polyamides condensed during processing ("RIM polyamide systems").

Examples of polyamides and copolyamides that can be used are derived from, *inter alia*, ϵ -caprolactam, adipic acid, sebacic acid, dodecanoic acid, isophthalic acid, terephthalic acid, hexamethylenediamine, tetramethylenediamine, 2-methyl-pentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, m-xylylenediamine or bis(3-methyl-4-aminocyclohexyl)methane; and also semi-aromatic polyamides such as polyamide 66/6I, for example consisting of 70 - 95 % polyamide 6/6 and 5 - 30 % polyamide 6/I; and also terpolymers in which some of the polyamide 6/6 has been replaced, for example consisting of 60 - 89 % polyamide 6/6, 5 - 30 % polyamide 6/I and 1 - 10 % of another aliphatic polyamide; the latter may con-

sist of, for example, polyamide 6, polyamide 11, polyamide 12 or polyamide 6/12 units. Such tricopolymers may accordingly be designated polyamide 66/6I/6, polyamide 66/6I/11, polyamide 66/6I/12, polyamide 66/6I/610 or polyamide 66/6I/612.

- 15 16. Polyureas, polyimides, polyamide imides, polyether imides, polyester imides, polyhydantoins and polybenzimidazoles.
17. Polyesters derived from dicarboxylic acids and dialcohols and/or from hydroxycarboxylic acids or the corresponding lactones, such as polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate, polyalkylene naphthalate (PAN) and polyhydroxy-benzoates, and also
10 block polyether esters derived from polyethers with hydroxyl terminal groups; and also polyesters modified with polycarbonates or MBS.
18. Polycarbonates and polyester carbonates.
19. Polyketones.
20. Polysulphones, polyether sulphones and polyether ketones.
- 15 20. Mixtures (polyblends) of the afore-mentioned polymers, for example PP/EPDM, polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6.6 and copolymers, PA/HDPE, PA/PP, PA/PPO, PBT/PC/ABS or PBT/PET/PC.
- 20 Preference is given to compositions wherein the thermoplastic polymer is polyethylene, polypropylene, high-impact polystyrene (HIPS), expandable polystyrene (EPS), expanded polystyrene (XPS), polyphenylene ether (PPE), polyamide, polyester, polycarbonate (PC) or a polymer blend of the type ABS (acrylonitrile-butadiene-styrene) or PC/ABS (polycarbonate/acrylonitrile-butadiene-styrene) or PPE/HIPS (polyphenylene ether/high-impact
25 polystyrene), especially a polyamide, polyester or a PPE/HIPS blend.

Special preference is given to polymer compositions according to the invention that comprise a filler or a reinforcing agent, e.g. filled polyethylene, polystyrene and especially talc filled polypropylene.

- 30 A preferred embodiment of the invention relates flame retardant composition, which comprises

A) A product as obtained by reaction of

- a) A tetrahydric alcohol selected from the group consisting of pentaerythritol and dipentaerythritol;
- b) A melamine compound selected from the group consisting of melamine phosphate and melamine pyrophosphate; and
- 5 c) A dendritic polymer of the polyester or polyamide type substituted by hydroxy groups, and

B) A thermoplastic polymer substrate.

A highly preferred embodiment relates to a flame retardant composition, which comprises

- A) A product as obtained by reaction of
 - 10 a) Pentaerythritol;
 - b) Melamine phosphate; and
 - c) A dendritic polyester formed from an initiator compound selected from the group consisting of trimethylolpropane, pentaerythritol and ethoxylated pentaerythritol and the chain-extending dimethylolpropionic acid or a poly-
15 condensation product of a cyclic carboxylic acid anhydride and diisopropylamine; and
- B) A thermoplastic polymer substrate selected from the group consisting of polyethylene, polypropylene and high impact polystyrene.

The instant invention further pertains to a composition, which comprises, in addition to the
20 product as obtained by reacting components a), b) and c), as defined above, d) further additives selected from the group consisting of polymer stabilizers and additional flame-retardants, such as phosphorus containing flame-retardants, further nitrogen containing flame-retardants, halogenated flame-retardants and inorganic flame-retardants.

Stabilizers are preferably halogen-free and selected from nitroxyl stabilizers, nitron stabilizers,
25 amine oxide stabilizers, benzofuranone stabilizers, phosphite and phosphonite stabilizers, quinone methide stabilizers and monoacrylate esters of 2,2'-alkylidenebisphenol stabilizers.

Additional flame-retardants as of present component d) are known components, items of commerce or can be obtained by known methods.

30 Representative phosphorus containing flame-retardants, in addition to the melamine compounds defined above with regard to component b), are for example:

Tetraphenyl resorcinol diphosphite (FYROLFLEX[®] RDP, Akzo Nobel), tetrakis(hydroxymethyl)phosphonium sulphide, triphenyl phosphate, diethyl-N,N-bis(2-hydroxyethyl)-aminomethyl phosphonate, hydroxyalkyl esters of phosphorus acids, ammonium polyphosphate (APP) or (HOSTAFLAM[®] AP750), resorcinol diphosphate oligomer (RDP), phosphazene
 5 flame-retardants and ethylenediamine diphosphate (EDAP).

Further nitrogen containing flame-retardants are, for example, isocyanurate flame-retardants, such as polyisocyanurate, esters of isocyanuric acid or isocyanurates. Representative examples are hydroxyalkyl isocyanurates, such as tris-(2-hydroxyethyl)isocyanurate, tris(hydroxymethyl)isocyanurate, tris(3-hydroxy-n-propyl)isocyanurate or triglycidyl isocyanurate.

10 Further examples are: benzoguanamine, tris(hydroxyethyl) isocyanurate, allantoin, glycoluril, melamine cyanurate, urea cyanurate or ammonium polyphosphate.

Representative organohalogen flame-retardants are, for example:

Polybrominated diphenyl oxide (DE-60F, Great Lakes Corp.), decabromodiphenyl oxide (DBDPO; SAYTEX[®] 102E), tris[3-bromo-2,2-bis(bromomethyl)propyl] phosphate (PB 370[®],
 15 FMC Corp.), tris(2,3-dibromopropyl)phosphate, tris(2,3-dichloropropyl)phosphate, chlorendic acid, tetrachlorophthalic acid, tetrabromophthalic acid, poly- β -chloroethyl triphosphonate mixture, bis(2,3-dibromopropyl ether) (PE68), brominated epoxy resin, ethylene-bis(tetrabromophthalimide) (SAYTEX[®] BT-93), bis(hexachlorocyclopentadieno)cyclooctane (DECLORANE PLUS[®]), chlorinated paraffins, octabromodiphenyl ether, hexachlorocyclopentadiene derivatives,
 20 1,2-bis(tribromophenoxy)ethane (FF680), tetrabromo-bisphenol A (SAYTEX[®] RB100), ethylene bis-(dibromo-norbornedicarboximide) (SAYTEX[®] BN-451), bis-(hexachlorocyclopentadieno) cyclooctane, PTFE, tris-(2,3-dibromopropyl)-isocyanurate, and ethylene-bis-tetrabromophthalimide.

The flame-retardant mentioned above routinely combined with inorganic (hydr)oxide synergists. Most common for this use are aluminum (hydr)oxide, such as $\text{Al}(\text{OH})_3$ or AlOOH , magnesium hydroxide, zinc or antimony oxides, e.g. Sb_2O_3 or Sb_2O_5 . Boron compounds and silicates are suitable, too.
 25

As mentioned above, the composition according to the invention may additionally contain one or more conventional additives, for example selected from pigments, dyes, plasticizers,
 30 antioxidants, thixotropic agents, levelling assistants, basic co-stabilizers, metal passivators, metal oxides, organophosphorus compounds, further light stabilizers and mixtures thereof, especially pigments, phenolic antioxidants, calcium stearate, zinc stearate, UV absorbers of the 2-hydroxy-benzophenone, 2-(2'-hydroxyphenyl)benzotriazole and/or 2-(2-hydroxyphenyl)-1,3,5-triazine groups.

A further embodiment of the invention relates to a process for the preparation of a melamine based flame retardant composition by reaction of a polyol and a melamine comprising compound, *characterized in that*

- 5 a) At least one polyol selected from the group consisting of a linear or branched, trihydric or tetrahydric alcohol, a linear pentahydric or hexahydric alcohol, a linear or cyclic C₄-C₆aldose and a linear or cyclic C₄-C₆ketose;
- b) At least one melamine comprising compound; and
- c) At least one dendritic polymer substituted by hydroxy groups;
- are reacted in the presence of polymers and, optionally, further processed.

10 The present invention accordingly relates also to the use of the flame retardants according to the invention for imparting flame-resistant properties to synthetic polymers, especially to thermoplastics, and also to a method of imparting flame-resistant properties to synthetic polymers, wherein at least one flame retardant according to the invention is incorporated in the synthetic polymers or is applied to their surface.

15 The incorporation of the reaction product which comprises components a), b) and c), as defined above, and optional further components into the polymer component B) is carried out by known methods such as dry blending in the form of a powder, or wet mixing in the form of solutions, dispersions or suspensions for example in an inert solvent, water or oil. The additive components a), b) and c) and optional further additives may be incorporated, for example, before or after molding or also by applying the dissolved or dispersed additive or additive mixture to the polymer material, with or without subsequent evaporation of the solvent or the suspension/dispersion agent. They may be added directly into the processing apparatus (e.g. extruders, internal mixers, etc.), e.g. as a dry mixture, pellets or powder, or as a solution or dispersion or suspension or melt.

25 The addition of the additive components to the polymer component B) can be carried out in all customary mixing machines in which the polymer is melted and mixed with the additives. Suitable machines are known to those skilled in the art. They are predominantly mixers, kneaders and extruders.

30 Particularly preferred processing machines are twin-screw extruders, e.g. contra-rotating or co-rotating twin-screw extruders. Other processing machines are planetary-gear extruders, ring extruders or co-kneaders. It is also possible to use processing machines provided with at least one gas or vapour removal compartment to which a vacuum can be applied.

Suitable extruders and kneaders are described, for example, in *Handbuch der Kunststoffextrusion*, Vol. 1 Grundlagen, Editors F. Hensen, W. Knappe, H. Potente, 1989, pp. 3-7, ISBN:3-446-14339-4 (Vol. 2 Extrusionsanlagen 1986, ISBN 3-446-14329-7).

For example, the screw length is 1 - 60 screw diameters, preferably 35-48 screw diameters.

- 5 The rotational speed of the screw is preferably 10 - 600 rotations per minute (rpm), very particularly preferably 25 - 300 rpm.

- The maximum throughput is dependent on the screw diameter, the rotational speed and the driving force. The process of the present invention can also be carried out at a level lower than maximum throughput by varying the parameters mentioned or employing weighing machines delivering dosage amounts.
- 10

If a plurality of components is added, these can be premixed or added individually.

The additive components a), b) and c) and optional further additives can also be added to the polymer in the form of a master batch ("concentrate"). In such operations, the polymer can be used in the form of powder, granules, solutions, and suspensions or in the form of lattices.

- 15 Incorporation can take place prior to or during the shaping operation. The materials containing the additives of the invention described herein preferably are used for the production of molded articles, for example roto-molded articles, injection molded articles, profiles and the like, and especially a fiber, spun melt non-woven, film or foam.

- Thus, present invention further pertains to molded or extruded articles, such as pipes, wire and cables, fibers, spun melt non-woven or a foam comprising the composition of the invention.
- 20

The following Examples illustrate the invention (percentages in weight percent):

Examples

Example 1: Referential Compositions according to WO2004/055029

5 Melamine phosphate (Melapur®, MP) and pentaerythritol are premixed in a high shear mixer at a molar ratio of 1.8 : 1.0. The premix obtained is fed to a twin-screw extruder ($\Phi=25$ mm; L/D=42; fitted with a vacuum degassing), which operates at a screw speed of 20-100 rotations per minute. Additional polypropylene (PP, Moplen®HF 500 N, Basell) is fed to the extruder in a PP concentration of 15 wt% (compare Table I). The average temperature in the extruder is 230-260°C, and the residence time is between 1 and 4 minutes, on average
10 2.5 minutes. To finalize the reaction between melamine phosphate and pentaerythritol, the extrudate obtained is cut into pellets and dried before carrying out a subsequent extrusion at 230-260°C.

Example 2: Inventive Compositions

15 Melamine phosphate, pentaerythritol, and the dendritic polymer substituted by hydroxy groups, component c), are premixed according to the values given in Table 1. The materials are processed in a manner analogous to the one of Example I.

Table 1: Composition of melamine based flame retardants

| Melamine based flame retardant Obtained according to | Stabilized Moplen® HF 500 N [%] | Penta-erythritol [%] | Melapur® MP [%] | Boltorn® H-20 [%] | Boltorn® H-30 [%] | Hybrane® P-1000 [%] |
|---|------------------------------------|-------------------------|--------------------|----------------------|----------------------|------------------------|
| Referential Composition 1 | 15 | 21.45 | 63.55 | - | - | - |
| Referential Composition 2 | 12.5 | 22.08 | 65.42 | - | - | - |
| Inventive Composition 1 | 15 | 20.71 | 61.36 | 2.93 | - | - |
| Inventive Composition 2 | 15 | 20.71 | 61.36 | - | - | 2.93 |
| Inventive Composition 3 | 12.5 | 24.54 | 60.59 | - | - | 2.37 |
| Inventive Composition 4 | 12.5 | 23.57 | 62.06 | - | - | 1.87 |
| Inventive Composition 5 | 12.5 | 23.57 | 62.06 | 1.87 | - | - |
| Inventive Composition 6 | 12.5 | 23.57 | 62.06 | - | 1.87 | - |

The pellets obtained according to Examples 1 and 2 are compounded in a twin-screw extruder ($\Phi=25$ mm; L/D=42) with pre-stabilized (0.3% IRGANOX B 225, 0.05% Ca-Stearate) PP (Moplen®HF 500 N) in such amounts that the resulting pellets contain 70% stabilized PP and 30% of the sum of components a) and b), according to the referential compositions, and components a), b) and c), according to the inventive compositions.

UL bars (1.6 mm) are prepared by injection molding of the pellets obtained. The UL 94-V test is carried out according to (DIN EN 60695-11-10). Additionally, after storage for one week in 70°C hot water (leaching test, compare UL 746C) the UL 94-V test is carried out. Table 2 contains the data for the weight loss due to the leaching test as well.

5 **Table 2: FR results before and after leaching test**

| Melamine based flame retardant Obtained according to | UL-94 Classification | Weight loss due to leaching [%] | % V-1 Classification according to UL-94 test after leaching | Burning time after first flaming (after leaching) [%] |
|--|----------------------|---------------------------------|---|---|
| Referential Composition 1 | V-0 | 11.5 | 0% V-1 | 677 |
| Referential Composition 2 | V-0 | 10.0 | 0% V-1 | 660 |
| Inventive Composition 1 | V-0 | 5.3 | 40% V-1 | 15 |
| Inventive Composition 2 | V-0 | 4.2 | 60% V-1 | 6 |
| Inventive Composition 3 | V-0 | 3.5 | 100% V-0 | 2 |
| Inventive Composition 4 | V-0 | 1.21 | 100% V-1 | 7 |
| Inventive Composition 5 | V-0 | 4.0 | 80% V-1 | 8 |
| Inventive Composition 6 | V-0 | 4.0 | 80% V-1 | 17 |

Before leaching all samples achieve the best UL-94 classification: V-0. In comparison with the Referential Compositions 1 and 2 all compositions according to the invention (Inventive Compositions 1-6) exhibit a significantly reduced weight loss due to leaching. The FR properties of the inventive compositions after leaching are improved, as reflected in the reduced values for the total burning times (5 bars, two times ignited) and the increased percentage (5 bars) of V-1 (according to UL-94) classification.

10

Claims

1. A product as obtained by reaction of:
 - a) At least one polyol selected from the group consisting of a linear or branched, trihydric or tetrahydric alcohol, a linear pentahydric or hexahydric alcohol, a linear or cyclic C₄-C₆aldose and a linear or cyclic C₄-C₆ketose;
 - b) At least one melamine comprising compound; and
 - c) At least one dendritic polymer substituted by hydroxy groups.
2. A product according to claim 1 as obtained by reaction of:
 - a) A linear or branched, trihydric or tetrahydric alcohol;
 - b) A melamine compound selected from the group consisting of melamine phosphate, melamine pyrophosphate and melamine polyphosphate; and
 - c) At least one dendritic polymer substituted by hydroxy groups.
3. A product according to claim 1 as obtained by reaction of:
 - a) A tetrahydric alcohol selected from the group consisting of pentaerythritol and dipentaerythritol;
 - b) A melamine compound selected from the group consisting of melamine phosphate, melamine pyrophosphate and melamine polyphosphate; and
 - c) A dendritic polymer of the polyester or polyamide type substituted by hydroxy groups.
4. A product according to claim 1 as obtained by reaction of:
 - a) A tetrahydric alcohol selected from the group consisting of pentaerythritol and dipentaerythritol;
 - b) A melamine compound selected from the group consisting of melamine phosphate and melamine pyrophosphate; and
 - c) A dendritic polymer of the polyester or polyamide type substituted by hydroxy groups.
5. A product according to claim 1 as obtained by reaction of:
 - a) Pentaerythritol;
 - b) Melamine phosphate; and

- c) A dendritic polyester formed from an initiator compound selected from the group consisting of trimethylolpropane, pentaerythritol and ethoxylated pentaerythritol and the chain-extending dimethylolpropionic acid or a polycondensation product of a cyclic carboxylic acid anhydride and diisopropanolamine.
- 5 6. A flame retardant composition according to claim 1, which comprises
- A) A product as obtained by reaction of:
- a) At least one polyol selected from the group consisting of a linear or branched, trihydric or tetrahydric alcohol, a linear pentahydric or hexahydric alcohol, a linear or cyclic C₄-C₆aldose and a linear or cyclic C₄-C₆ketose;
- 10 b) At least one melamine comprising compound; and
- c) At least one dendritic polymer substituted by hydroxy groups; and
- B) A polymer substrate.
7. A flame retardant composition according to claim 6, which comprises
- A) A product as obtained by reaction of
- 15 a) A tetrahydric alcohol selected from the group consisting of pentaerythritol and dipentaerythritol;
- b) A melamine compound selected from the group consisting of melamine phosphate and melamine pyrophosphate; and
- c) A dendritic polymer of the polyester or polyamide type substituted by hydroxy groups, and
- 20 B) A thermoplastic polymer substrate.
8. A flame retardant composition according to claim 6, which comprises
- A) A product as obtained by reaction of
- a) Pentaerythritol;
- 25 b) Melamine phosphate; and
- c) A dendritic polyester formed from an initiator compound selected from the group consisting of trimethylolpropane, pentaerythritol and ethoxylated pentaerythritol and the chain-extending dimethylolpropionic acid or a polycondensation product of a cyclic carboxylic acid anhydride and diisopropanolamine; and
- 30

- B) A thermoplastic polymer substrate selected from the group consisting of polyethylene, polypropylene and high impact polystyrene.
9. A flame retardant composition according to claim 6, which comprises d) further additives in addition to components a), b) and c) selected from the group consisting of polymer stabilizers and additional flame-retardants.
- 5
10. Formed articles comprising the flame retardant composition according to claim 6.
11. A process for the preparation of a melamine-based flame retardant composition by reaction of a polyol and a melamine comprising compound,
characterized in that
- 10
- a) At least one polyol selected from the group consisting of a linear or branched, trihydric or tetrahydric alcohol, a linear pentahydric or hexahydric alcohol, a linear or cyclic C₄-C₆aldose and a linear or cyclic C₄-C₆ketose;
- b) At least one melamine comprising compound; and
- c) At least one dendritic polymer substituted by hydroxy groups;
- 15
- are reacted in the presence of polymers.
12. A process according to claim 11, *characterized in that* components a), b) and c) are reacted in the presence of thermoplastic polymers by reactive extrusion methods.
13. A process according to claim 12, *characterized in that* components a), b) and c) are reacted in the presence of thermoplastic polymers in a twin-screw extruder.
- 20
14. A process for imparting flame retardancy to a polymer, which process comprises the incorporation of a product according to claim 1 to the polymer.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/063159

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08L101/00 C08K5/3492

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| A | WO 2004/055029 A2 (CIBA SC HOLDING AG [CH]; WANG QI [CN]; CHEN YINGHONG [CN]; LIU YUAN [C]) 1 July 2004 (2004-07-01) cited in the application page 2, paragraph 2 - page 7, paragraph 4; claims; examples | 1-14 |

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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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INTERNATIONAL SEARCH REPORT

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| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
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Information on patent family members

International application No

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